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(N-{2-[(2-Aminoethyl)amino]ethyl}salicylideneaminato-O,N,N',N'')aquacopper(II) Hexafluorophosphate, [Cu(C₁₁H₁₆N₃O)(H₂O)]PF₆

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Abstract. $M_r = 432 \cdot 8$, monoclinic, $P2_1/c$, $a = 10 \cdot 182$ (2), $b = 14 \cdot 863$ (3), $c = 11 \cdot 188$ (2) Å, $\beta = 98 \cdot 6$ (1)°, $U = 1674 \cdot 1$ (7) Å³, $Z = 4$, $D_x = 1 \cdot 717$ g cm⁻³, $\lambda(\text{Mo } K\alpha) = 0 \cdot 71069$ Å, $F(000) = 876$, final $R = 0 \cdot 085$ and $R_w = 0 \cdot 089$ for 1406 reflections. The coordination polyhedron around Cu is a square pyramid with the saldien ligand coordinated in the basal plane through one O and three N atoms; the apical position is occupied by the O of the water molecule; the Cu atom is displaced $0 \cdot 174$ (2) Å from the equatorial plane toward the water molecule.

Introduction. In recent years a great deal of attention has been given to salicylideneaminato derivatives of transition metals and their structural, electronic and magnetic properties have been measured and explained in depth. This interest can be connected both to the electronic and structural similarity of salicylaldehyde and pyridoxal (vitamin B_6 coenzyme) derivatives (Snell, Fasella, Bramestein & Rossi Fanelli, 1963) and to the oxygenation ability of some 'oxygen-carrier' salicylideneaminato complexes (Floriani & Calderazzo, 1969; Crumblis & Basolo, 1970).

Schiff-base complexes, therefore, have been suggested as models to describe energy transfer in naturally occurring systems and the role of the coordination sphere about the metal ion in determining the nature of the model system has been greatly emphasized (Wilkins, 1971). We have recently described the kinetic template effect of Cu[II] in the reaction of the salicylaldehydato

ion with diethylenetriamine (Rotondo & Cusmano Priolo, 1982): as a consequence of the presence of Cu[II], the reaction between the ligands leads to the monoimine derivative through a first-order kinetic process occurring within the coordination sphere of the metal. The peculiarity of the proposed mechanism together with the nature of the title compound, which is, to our knowledge, the first example of a diethylenetriamine with only one of its NH_2 groups condensed with the carbonyl, suggested the undertaking of the crystal structure determination of this compound.

Crystal structure determinations of analogous Ni[II] and Co[II] derivatives are in progress.

Experimental. A methanolic solution of dien added to 241 mg of $Cu(NO_3)_2.3H_2O$ in water; the mixture allowed to stand for several days at room temperature, a saturated solution of KPF_6 in water then added; slow evaporation of the solvent leads to the formation of dark-violet crystals of the monoimino derivative. The analytical data (wt %) with the calculated values in parentheses and the characteristic IR bands (cm⁻¹) are: C $30 \cdot 60$ ($30 \cdot 52$), H $4 \cdot 22$ ($4 \cdot 16$), N $9 \cdot 55$ ($9 \cdot 71$), ν(OH) 3640, ν(NH) 3358, 3315, 3150 (*br*), ν(C=N) imino 1640, (PF) 850 *vs* (*br*). The ν(OH) stretching frequency of 3640 cm⁻¹ is sharp and supports the absence of hydrogen-bonding interactions. Prismatic crystal $0 \cdot 10 \times 0 \cdot 12 \times 0 \cdot 14$ mm: 25 reflections with $8 < \theta < 12°$ used for measuring lattice parameters; two standard reflections measured every 120 min, no significant

intensity variation; 2156 independent reflections collected on a Siemens–Stoe four-circle diffractometer ($3° < \theta < 25°$) with ω/θ scan mode, 1406 with $I > 2\cdot5\sigma(I)$; Lp correction, absorption ignored; structure solved by Patterson and Fourier methods and refined by full-matrix least-squares techniques; H atoms, except those of the coordinated water molecule, introduced at calculated positions (C—H 0·95 Å) with isotropic $U = 8\cdot0$ Å^2; anisotropic temperature factors assigned to the non-hydrogen atoms; weighting scheme $3\cdot0337/\sigma^2(F_o) + 0\cdot001172(F_o)^2$ used in the last refinement cycles, final $R = 0\cdot085$, $R_w = 0\cdot089$;* atomic scattering factors (corrected for anomalous dispersion of Mo) taken from *International Tables for X-ray Crystallography* (1974); no peaks higher than 0·5 e Å^{-3} in the final difference Fourier map with the highest values in the proximity of the PF$_6$ group; computations were carried out using the *SHELX* system (Sheldrick, 1976) on an IBM 4331 computer.

Discussion. The structure consists of distinct cations and anions separated by van der Waals distances, as shown by the packing arrangement of Fig. 1. Table 1 gives the final atomic parameters and Table 2 bond lengths and angles. The four basal atoms lie roughly in a plane [the deviations from the best mean plane through them being N(1) −0·043 (12), N(2) 0·034 (10), N(3) −0·042 (12), O(1) 0·030 (10) Å]. The Cu atom is displaced with respect to the basal plane by 0·174 (2) Å towards the apical position, while the C atoms of the aliphatic chains are symmetrically displaced from the same plane in the opposite direction: C(1) −0·003 (16), C(2) −0·603 (16), C(3) −0·635 (15), and C(4) −0·073 (16) Å.

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* Lists of structure factors, anisotropic thermal parameters and H-atom coordinates have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38331 (12 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.
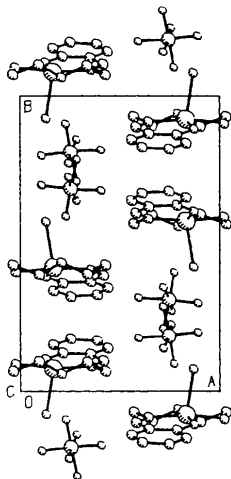

Fig. 1. Projection of the structure onto the $x\,y$ plane.

Table 1. *Atomic coordinates* ($\times 10^4$) *and equivalent isotropic thermal parameters* (Å$^2 \times 10^2$) *for non-hydrogen atoms, with e.s.d.'s in parentheses*

$$U_{eq} = \tfrac{1}{3}\textstyle\sum_i\sum_j U_{ij}d_i^*d_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
Cu	1660 (2)	788 (1)	1386 (1)	4·2 (1)
O(1)	1299 (9)	1126 (7)	−255 (9)	5·3 (6)
O(2)	1300 (9)	−777 (7)	1037 (9)	5·9 (6)
N(1)	3547 (11)	872 (8)	1478 (11)	4·4 (7)
N(2)	2069 (12)	615 (7)	3199 (10)	4·9 (7)
N(3)	−206 (13)	939 (8)	1703 (11)	5·7 (8)
C(1)	−298 (17)	736 (11)	2972 (14)	6·9 (11)
C(2)	929 (17)	1006 (11)	3745 (13)	6·2 (11)
C(3)	3352 (18)	989 (10)	3561 (13)	6·5 (11)
C(4)	4291 (16)	704 (11)	2672 (15)	6·9 (10)
C(5)	3997 (13)	1058 (8)	563 (13)	7·1 (13)
C(6)	3524 (16)	1275 (10)	−681 (14)	5·3 (10)
C(7)	4365 (16)	1497 (10)	−1539 (17)	6·0 (11)
C(8)	3871 (22)	1741 (12)	−2697 (17)	7·7 (11)
C(9)	2535 (20)	1780 (11)	−3003 (15)	6·2 (11)
C(10)	1683 (16)	1579 (10)	−2202 (13)	5·5 (10)
C(11)	2125 (15)	1310 (9)	−1033 (14)	4·5 (10)
P	2526 (4)	−1894 (3)	4533 (4)	5·7 (3)
F(1)	2822 (12)	−2873 (8)	4129 (12)	11 (1)
F(2)	4110 (15)	−1893 (13)	4912 (15)	18 (2)
F(3)	2188 (25)	−971 (7)	4956 (18)	22 (2)
F(4)	1100 (14)	−2038 (13)	4112 (22)	25 (2)
F(5)	2392 (20)	−2267 (10)	5784 (14)	17 (2)
F(6)	2804 (16)	−1464 (9)	3296 (10)	14 (1)

Table 2. *Bond lengths* (Å) *and angles* (°) *with e.s.d.'s in parentheses*

Cu O(1)	1·89 (1)	Cu O(2)	2·38 (1)
Cu—N(2)	2·02 (1)	Cu—N(3)	2·00 (1)
Cu—N(1)	1·91 (1)		
C(1)—C(2)	1·47 (2)	C(3)—C(4)	1·54 (2)
N(3)—C(1)	1·47 (2)	N(2)—C(2)	1·51 (2)
N(2)—C(3)	1·42 (2)	N(1)—C(4)	1·46 (2)
N(1)—C(5)	1·21 (2)	O(1)—C(11)	1·33 (2)
C(5)—C(6)	1·44 (2)	C(6)—C(7)	1·42 (2)
C(7)—C(8)	1·37 (2)	C(8)—C(9)	1·35 (3)
C(9)—C(10)	1·37 (2)	C(10)—C(11)	1·38 (2)
C(6)—C(11)	1·42 (2)		
P(1)—F(1)	1·57 (1)	P(1)—F(3)	1·51 (1)
P(1)—F(2)	1·60 (2)	P(1)—F(4)	1·47 (1)
P(1)—F(5)	1·53 (1)	P(1)—F(6)	1·59 (1)
O(2)—Cu—O(1)	95·6 (4)	O(2)—Cu—N(1)	101·6 (4)
O(2)—Cu—N(2)	92·5 (4)	O(2)—Cu—N(3)	90·7 (5)
O(1)—Cu—N(1)	94·7 (5)	N(1)—Cu—N(2)	84·2 (5)
N(2)—Cu—N(3)	84·0 (5)	N(3)—Cu—O(1)	95·2 (5)
N(3)—Cu—N(1)	163·3 (5)	O(1)—Cu—N(2)	171·8 (5)
Cu—N(3)—C(1)	110 (1)	N(3)—C(1)—C(2)	110 (2)
C(1)—C(2)—N(2)	107 (1)	C(2)—N(2)—C(3)	118 (1)
Cu—N(2)—C(2)	108	Cu—N(2)—C(3)	106 (1)
N(2)—C(3)—C(4)	110 (1)	C(3)—C(4)—N(1)	105 (1)
C(4)—N(1)—Cu	115 (1)	Cu—N(1)—C(5)	118 (1)
C(4)—N(1)—C(5)	127 (1)	N(1)—C(5)—C(6)	139 (1)
C(5)—C(6)—C(11)	117 (2)	C(6)—C(11)—O(1)	121 (2)
C(5)—C(6)—C(7)	124 (2)	O(1)—C(11)—C(10)	122 (2)
C(11)—O(1)—Cu	130 (1)	C(11)—C(10)—C(9)	122 (2)
C(6)—C(11)—C(10)	116 (1)	C(9)—C(8)—C(7)	118 (2)
C(10)—C(9)—C(8)	122 (2)	C(7)—C(6)—C(11)	119 (2)
C(8)—C(7)—C(6)	122 (2)		
F(1)—P—F(3)	177 (1)	F(2)—P—F(4)	171 (1)
F(5)—P—F(6)	174 (1)		

The conformation along with the helicity (IUPAC, 1970) adopted by the chelate rings are as follows:

Ring	Conformation	Helicity
N(3) —Cu— N(2)	Envelope (or *gauche*)	λ
N(2) —Cu— N(1)	Envelope (or *gauche*)	δ
N(1) —Cu— O(1)	Nearly planar with boat deformation	Non-helical.

The three Cu—N bonds are not equivalent: two Cu—N(amine) bond distances [Cu—N(2) and Cu—N(3)] are comparable while the third [Cu—N(1)] is significantly shorter and comparable with the Cu—O(1) bond distance in the basal plane.
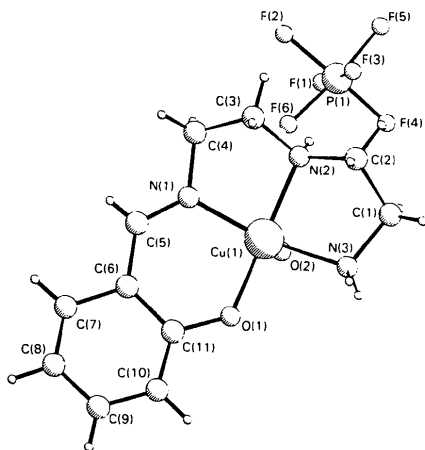
The coordination polyhedron around Cu is a square pyramid whose base is formed by one O and three N atoms from the saldien ligand; the apical position is occupied by the O atom of a water molecule bound to metal as shown in Fig. 2, which represents a view of the asymmetric unit projected onto the saldien plane.

The Cu—O(2)(water) bond distance compares well with the value $2 \cdot 359$ (8) Å found in aqua[3,6-bis(2-pyridyl)pyridazine]trichlorohydroxodicopper(II) (Ghedini, De Munno, Denti, Manotti Lanfredi & Tiripicchio, 1982) for a similar distance. Bond distances and angles in the ligand are in agreement with those reported in analogous compounds.

Fig. 2. The asymmetric unit projected onto the saldien plane.

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Structure of Bis(tetraphenylphosphonium) Tris[chlorocopper(I)]tetrathiomolybdate(VI)* Methyl Cyanide Solvate, [Ph₄P]₂[MoS₄(CuCl)₃].CH₃CN

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Abstract. $M_r = 1241 \cdot 0$, monoclinic, $P2/n$, $a = 17 \cdot 044$ (2), $b = 13 \cdot 546$ (2), $c = 22 \cdot 826$ (3) Å, $\beta = 96 \cdot 46$ (1)°, $U = 5236 \cdot 6$ Å³, $Z = 4$, $D_x = 1 \cdot 574$ Mg m⁻³; Mo $K\alpha$ radiation, $\lambda = 0 \cdot 71069$ Å, $\mu = 1 \cdot 84$ mm⁻¹, $F(000) = 2495 \cdot 5$, $T = 291$ K; $R = 0 \cdot 068$ for 6091 reflections. The two crystallographically independent anions lie on twofold axes; each consists of an essentially tetrahedral MoS₄ arrangement, for which three of the six S···S edges are bridged by CuCl.

* IUPAC name:bis(tetraphenylphosphonium) [1,2,3-trichloro-1,2;2,3-di-µ-thio-1,3-dithiotricuprato(I)-S^1,S^2,S^3,S^4]molybdate(2−).